

Molecular tuning of the magnetic response in organic semiconductors

Erik R. McNellis,^{1,*} Sam Schott,² Henning Sirringhaus,² and Jairo Sinova¹¹*INSPIRE Group, Johannes Gutenberg University, Staudingerweg 7, D-55128 Mainz, Germany*²*Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom*

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We demonstrate an extreme variability and tunability of the molecular gyromagnetic coupling g -tensor with respect to the geometric and electronic structure in a much studied class of organic semiconductors (OSCs). This class of OSCs is composed of a structural theme of phenyl- and chalcogenophene (group XVI element containing, five-membered) rings and alkyl functional groups, and it forms the basis of several intensely studied high-mobility polymers and molecular OSCs. We show how in this class the g -tensor shifts, Δg , are determined by the effective molecular spin-orbit coupling (SOC), defined by the overlap of the atomic spin density and the heavy atoms in the polymers. We explain the dramatic variations in SOC with molecular geometry, chemical composition, functionalization, and charge dwell time, by using a first-principles theoretical model based on atomic spin populations. Our approach guides the tuning of the magnetic response of these and other OSCs by chemical synthesis.

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I. INTRODUCTION

A key goal of spintronic materials design is to tune the interactions between electronic spins, electronic motion, and fields present in the material. We have shown in a previous publication [1] that the gyromagnetic coupling (“ g -”) tensor in a class of high-mobility organic semiconductors (OSCs) almost exclusively depends on the molecular spin-orbit coupling (SOC), which in turn depends on the molecular spin density distribution. The latter, and therefore the g -tensor, can be tuned via chemical composition and substitution, molecular geometry, and functionalization.

An essential step in our analysis is the development of a first-principles theoretical model to guide the engineering of g -tensors in OSCs. In this contribution, we complete this theoretical model by extending it to a range of yet experimentally unexplored molecules, validating the applicability and transferability of our approach, and extending it to include charge dwell-time effects.

As in related efforts in molecular electronics [2], photonics and photovoltaics [3], the expected benefits of crafting spintronic devices from molecules [4] include reduced cost of production, increased material tailorability and abundance, and disruptive technologies outperforming traditional components in given areas, such as OLEDs. Molecular spintronics holds great potential in long spin lifetime, hybrid organic-inorganic designs [5], and is central to the concept of using molecules to tune solid interfaces for spintronic applications, so-called “spinterfaces” [6,7]. Although spintronic phenomena in solid state and in molecules share the common origins of spin-orbit coupling and hyperfine fields, the difference in environment and geometry of the two types of systems can give rise to very different spin physics.

For example, molecular SOC must be understood as more generally dependent on electronic and geometric structure than SOC in solid state materials. While molecular SOC may be tuned by substitution with heavier elements, analogous to doping in solid state materials, the influence of chemical composition on the SOC of light molecules may be weaker than, e.g., aspects of molecular geometry or charge distribution [8].

In our recent work [1], we focused on a class of chalcogenophene (five-membered rings composed of carbon and a single group XVI atom) based OSCs with an [1]benzothieno[3,2-*b*][1]-benzothiophene (BTBT) molecule as the central structural element (see Fig. 1). We found g -tensor shifts (Δg) in this class sensitive to molecular composition and structure to a degree running counter to established chemical intuition. The unexpectedly strong variations of Δg highlight the great potential for purposeful tuning of these and similar molecular spintronic components. However, to reach this potential and resolve the complex relationship between molecular structure and composition, spin density, SOC and Δg for (in principle) any OSC molecules, a clear computational recipe must be defined and validated for a larger class of molecules.

BTBT consists of two fused thiophene (C_4S) rings extended by fused phenyl (C_6H_4) moieties on opposite sides. While BTBT and its synthesis has been known since 1949, [9] its potential as a high-mobility ($\mu > 1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) OSC has only recently been realized. The basic structural theme of a conjugated molecule consisting of one or several chalcogenophene- and phenyl-rings, functionalized with alkyl chains for improved solubility and thin-film morphology, has come to form a class of high mobility OSCs [10].

Compositional variations in this class include substitutions with heavier chalcogens, functionalization with alkyl chains, and extension of the conjugation length by adding fused phenyl rings. Substituting the thiophene rings in BTBT for

*emcnelli@uni-mainz.de

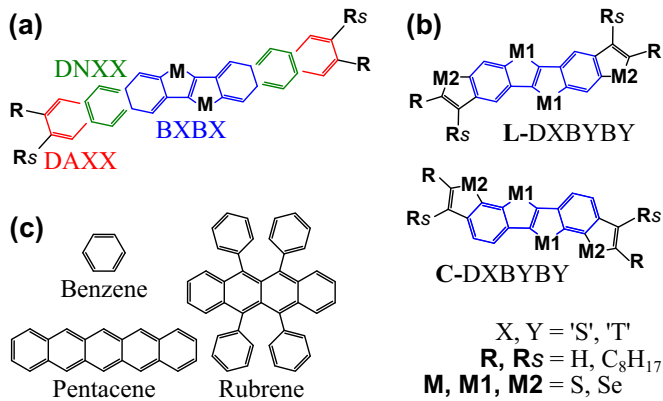


FIG. 1. Structural formulas of all molecules studied in this work. (a) Single chalcogen pair molecules, with the central BXB X ($X = \text{"T"}$ and "S" for $M = \text{sulfur}$ and selenium , respectively) structure shown in blue. Adding one and two sets of fused phenyl rings gives DNXX (green) and DAXX (red), respectively. Further shown is the bonding site of the C8 alkyl chain functional group (R), and that same group shifted to the adjacent bonding site (R_s). (b) Linear (L) and curved (C) dual chalcogen pair molecules DXBYBY, including the mixed pair DSBTBT molecules, where $M1 = \text{sulfur}$ and $M2 = \text{selenium}$. Otherwise with nomenclature and functionalization as in (a). (c) The pure hydrocarbons benzene, rubrene, and pentacene included for improved fit quality.

selenophene produces the “BSBS” analog [11]. Alkylation is generally done to improve solubility and thin-film morphology, with molecules with n -membered chains labeled C_n -X (e.g., “C8-BTBT”) [12,13]. Substituting the single phenyl ring (“benzo-”) moieties in BTBT for double ring (“dinaphta-”) moieties yields the so-called DNTT molecule [14]. The same molecule with a three ring (“dianthra-”) moiety is called DATT [10]. The Se-substituted analogues of DNTT and DATT are labeled DNSS and DASS, respectively. Some of these compounds have been employed as high-mobility organic field-effect and thin-film transistors (OFETs and OTFTs) [13,15].

However, minor variations in composition can produce significantly lower hole mobilities, which has been attributed to the large differences in HOMO orbital weight on the chalcogen atoms observed in first-principles calculations [11]. This aligns very well with our own finding that the tunability of magnetic response with structural variations of these molecules can be attributed to the corresponding variation of spin density weight at the chalcogen atoms [1].

A conceptually similar approach of tuning molecular magnetic properties by chalcogen substitution and analyzing the result in terms of spin densities calculated using first-principles theoretical methods has already been employed by Winter *et al.* [16,17], albeit for different systems and properties.

The structural theme of chalcogenophenes and alkyl functional groups also forms the basis of many intensively studied high-mobility polymers, such as PBTBT [18] and P3HT [19]. While these remain outside the scope of this work, we expect our key insights to also be valid for such polymers.

This paper is organized as follows. In Sec. II, we describe the set of molecules studied in greater detail, followed by a presentation of a simple model devised to describe the

relationship between g -tensor shifts and the molecular spin density distribution. This model is parametrized by electronic structure calculations from first-principles theory, the methodological detail of which is explained in the following subsection. All first-principles results, as well as the quality and applicability of our g -tensor shift model, are presented and discussed in context in Sec. III, and finally summarized in Sec. IV.

II. STUDIED MOLECULES AND METHODOLOGY

A. Target class of OSC molecules

The set of chalcogenophene OSCs studied here is illustrated using structural formulas in Fig. 1. The BXB X molecule is shown in blue in Fig. 1(a) ($X = \text{"T"}$ and "S" for sulfur and selenium chalcogens, respectively), along with its extension of the fused phenyl moieties to DNXX and DAXX, forming a total of three basic chalcogenophene structures with a single chalcogen atom pair. Further shown is the position of the eight-membered alkyl chain (C_8H_{17} —) functional group R . This is generally how these molecules have been alkylated in literature [10,12,13]. However, as will be shown below, the spin density weight on the conjugated moiety at the alkyl chain bonding site modifies the influence of the functional group on the g -tensor shift. In most of the molecules studied here, there is a spin density maximum on the conjugated moiety at the bonding site R in Fig. 1, and a minimum at the adjacent, “shifted” site of R_s . This is illustrated in Fig. 2. Consequentially, we also include molecules functionalized at the shifted bonding site in our target class. All combinations of the three single chalcogen pair molecules with the three possibilities of no alkyl chain, alkylation at the ordinary and shifted sites amount to nine sulfur-based molecules, which with their selenium-substituted analogues add up to 18 molecules.

The next variation of the BXB X structural motif is shown in Fig. 1(b)—the incorporation of a second set of chalcogenophene rings. These can be added forming a linear shape with, e.g., the BTBT molecule, which we denote L-DTBTBT (“dibenzothiopheno[6,5-b:6',5'-f]thieno[3,2-b]thiophene”), or forming a curved “S” shape (“dibenzothiopheno[7,6-b:7',6'-f]thieno[3,2-b]thiophene”), which we correspondingly label C-DTBTBT. We include all variations of selenium substitutions (e.g., “L-DSBSBS”), no alkylation and alkylation at the two possible sites, for a total of twelve distinct molecules added to the preceding 18. Additionally, as a way of cross-referencing the sulfur and selenium fits, we add the latter set with an inner sulfur- and outer selenium-atom pairs, e.g., L-DSBTBT, which with the curved and linear forms and the three alkylation options add a further six molecules to the 30 already described.

Finally, in order to improve the quality of the fitted carbon atom coefficients, the chalcogen-free hydrocarbons benzene, pentacene, and rubrene are included in the fit, for a total of 39 distinct molecules. Structural formulas of the latter are shown in Fig. 1(c).

The point-group symmetries of the neutral molecules here are D_{6h} for benzene, D_{2h} for rubrene and pentacene, and C_{2h} for all chalcogenophenes. As further explained in subsection IIID, the calculation of charge dwell-time effects requires the calculation of properties also in the relaxed cationic geometry.

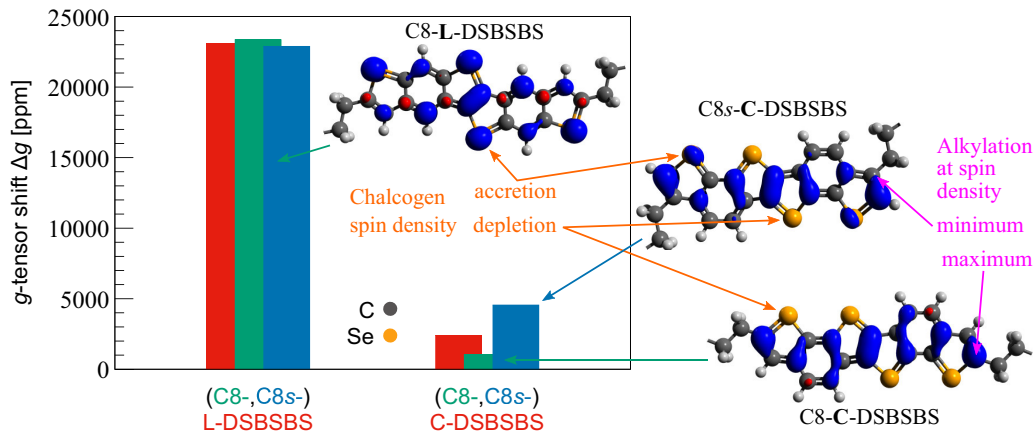


FIG. 2. Illustration of the relationship between predicted g -tensors and molecular spin density distributions, and the variations of the latter with molecular geometry and functionalization. At left (right), the histogram shows calculated Δg for the linear (curved) DSBSBS molecules without alkyl chains, and C8/C8s alkyl chains bonded at spin density maxima and minima. As shown by the blue isocontour in the accompanying spin density plots, the L-DSBSBS molecule has heavy spin density weight at the chalcogen atoms— Δg is large. The spin density structure is not significantly changed when alkylating L-DSBSBS at the two sites. The *opposite* is true in the C-DSBSBS molecule, *despite its identical chemical composition*: alkylating C-DSBSBS at a bonding site corresponding to a spin density maximum (C8-C-DSBSBS) pulls spin density away from all chalcogens, whereas alkylating at a spin density minimum (C8s-C-DSBSBS) leaves significant weight on the outer chalcogen pair. Qualitatively similar variations are found in all other molecules studied here.

The difference between the neutral and cationic geometries may be substantial, to the extent of changing the point-group symmetry. Among the molecules studied here, this only occurs in benzene, which reduces to D_{2h} in the cationic state.

B. Ansatz for molecular SOC: g -tensor linearly dependent on atomic spins

We begin by briefly summarizing the g -tensor theory underpinning this work. Following Stone [20] in the Neese formulation [21], the gauge-invariant molecular g -tensor can be written as

$$\mathbf{g} = g_e + \Delta \mathbf{g}^{\text{RMC}} + \Delta \mathbf{g}^{\text{GC}} + \Delta \mathbf{g}^{\text{OZ/SOC}}, \quad (1)$$

where g_e is the scalar Landé g -factor of free electrons, and the next three terms form the rank 2, 3×3 shift tensor $\Delta \mathbf{g}$, which averaged over its Cartesian components yields the isotropic shift Δg . The first two terms of $\Delta \mathbf{g}$ are a relativistic mass correction and gauge correction, respectively, and the last is a mixed second derivative of the total energy, with contributions from the orbital Zeeman and SOC terms.

The relative magnitudes of the three terms in the studied class of molecules are a crucial point in our reasoning. Relativistic effects, to include mass corrections, are generally small in organic molecules. If also the gauge correction is sufficiently small, the molecular g -tensor shifts Δg are dominated by $\Delta g^{\text{OZ/SOC}}$, in turn making the molecular SOC the tuning parameter determining Δg . As will be shown in Sec. III, this is indeed the case for our target molecules. A stronger influence of the first two terms is however perfectly possible, depending on the molecular chemical composition. In practice, relative magnitudes of the Δg terms must be heuristically determined.

$\Delta g^{\text{OZ/SOC}}$ is linear in the molecular SOC, which is dominated by one-electron scalar products between electronic spins and molecular orbital angular momentum. Many-body terms such as the two-body spin-spin-orbit (SSO) and spin-

other-orbit (SOO) interactions also contribute, but to a significantly lesser degree. Since SOC is weak on the scale of other electronic interactions, and the two-body SOC terms therefore usually negligible, SOC is often modeled as a local operator in solid state systems. If its spin density can be sufficiently well approximated as a sum of atomic contributions, this approximation holds also for a molecule. In order to compare differences in molecular SOC between molecules of differing geometry and composition, we therefore make the ansatz that $\Delta g^{\text{OZ/SOC}}$ is linear in the molecular spin density, approximated as a sum of localized atomic spins, with element-dependent proportionality constants representing the net orbital angular momentum interaction.

That is, we make the approximation

$$\Delta g^{\text{OZ/SOC}} \approx \sum_{e=1}^M c_e \sum_{i=1}^N \sigma_i^e, \quad (2)$$

where σ_i^e is the effective spin at atom i of element e , N is the number of atoms of element e in the molecule, M is the number of different elements, and c_e a constant. While such localized approximations of SOC are common in solid-state models [22], their utility for molecules is considerably less obvious. The key benefit of this approximation is that it casts changes in the (here) dominant part of the molecular g -tensor shift in terms of changes in the molecular spin density, which is readily obtained.

This approach is not the first to postulate a strong relationship between the magnitudes of Δg and the molecular SOC. Yu [23] derived Δg solely in terms of the up-down spin admixture parameter γ , which is the first order approximation of SOC from perturbation theory [23,24]. γ omits the magnetic field response term of $\Delta g^{\text{OZ/SOC}}$. We tentatively suggest this as the reason why test calculations using Yu's technique failed to produce results comparable to either our experimental or theoretical numbers. Since this is outside the scope of the

current contribution, we will further explore the relationship between γ and Δg in a future publication.

We cannot expect universal transferability of a localized approximation on the form of Eq. (2). However, if our Ansatz holds sufficiently well within a given class of molecules, we may fit common c_e for that class, and analyze internal variations in terms of the spin density distribution (magnitude of atomic spins). In the following, we approximate $\Delta g^{\text{OZ/SOC}}$ for a target molecule by (a) calculating atomic spins σ_i^e for a given set of molecules including the target molecule, (b) fitting c_e coefficients to DFT $\Delta g^{\text{OZ/SOC}}$ terms for the set excluding the target molecule, and (c) evaluating Eq. (2) with the target σ_i^e . This way, the target molecule is not part of its own c_e fitting set.

Since a negative c_e lacks physical interpretation, we use a non-negative multivariate least-squares fitting algorithm implemented in SCIENTIFIC PYTHON [25] (version 0.16.1, using subroutine `scipy.optimize.nnls`). Since their maximal atomic orbital momentum is zero, hydrogen atoms were excluded from the c_e fits. As a simple but commonplace statistical test, we calculate the coefficient of determination or R^2 value according to

$$R^2 \equiv 1 - \frac{SS_{\text{res}}}{SS_{\text{tot}}} = 1 - \frac{\sum_i (x_i - y_i)^2}{\sum_i (x_i - \bar{x})^2}, \quad (3)$$

where SS_{res} , SS_{tot} , x_i , and y_i are the residual sum of squares, the total sum of squares, and the calculated and fitted $\Delta g^{\text{OZ/SOC}}$ value, respectively.

C. DFT calculations: geometries, g -tensors, spin densities

We use density functional theory (DFT) to calculate molecular geometries, g -tensors, and atomic spin densities. Describing SOC effects in organic molecules from first-principles theory is challenging, since they are generally small but often not negligible. The standard approach of spin-orbit DFT (SODFT)—describing SOC as a correction to a scalar relativistic effective core potential (ECP) [26]—is well justified for heavy atoms, with deep cores decoupled from the chemical bonding of the valence electrons, and interacting weakly with the chemical environment.

However, in lighter elements, the frozen-core approximation of an ECP is much more spurious, both in terms of SOC and other electronic interactions. We therefore opt for an all-electron SODFT treatment, with nuclear relativistic effects described by the zeroth-order regular approximation [27] (ZORA) with the standard point-charge approximation of atomic nuclei. We chose the high-quality SARC [28] basis set family, which has been recontracted for the ZORA approximation, testing singly and doubly polarized valence sets from single- (SVP) to quadruple-zeta (QZVP / QZVPP) sizes. In so doing, we were forced to remove the two diffuse (augmentation) functions on the carbon atoms in order to eliminate linear dependencies, but no other modifications to the basis sets were made. Geometries were found fully converged with respect to basis set size at triple-zeta (TZVP) level, but g -tensor shifts increased slightly (<300 ppm) at quadruple-zeta level, worsening the comparison to experimental measurements, which indicates that the quality of TZVP g -tensor

shift predictions is partly due to cancellation between basis set and other errors.

Deficiencies due to electron delocalization error [29] in (semi-) local exchange-correlation (xc) DFT functionals are particularly severe for molecules [30] and magnetic phenomena. Therefore hybrid xc functionals, with nonlocal exact exchange added to the (semi-)local terms, perform better for the calculation of g -tensors [31]. All calculations presented here were performed using the PBE0 [32] hybrid xc-functional, which has been shown [33] to perform excellently for similar systems, including almost reproducing [34] the G_0W_0 band structure of pentacene and rubrene.

All calculations were performed on single molecules, approximating molecules dissolved in solution. All g -tensor calculations were performed on positively charged (cationic) molecules. For each molecule, the geometry was obtained by unrestricted geometry optimization in the charge neutral and cationic states, simulating the limits of short and long lifetime of the charged state (i.e., the charge dwell time), respectively. All geometry optimizations were carried out using the NWChem quantum chemistry software, version 6.5 [35].

g -tensors of cationic molecules were calculated using optimized geometries at the exact same level of theory, using the coupled-perturbed Kohn-Sham technique [33] and SOC operator approximation [36] developed by Neese, and implemented in the ORCA software package [37], version 3.0.3.

Calculating atomic spins from molecular spin densities in a consistent and transferable manner is difficult, since it requires a solution to the atoms-in-molecules (AIM) problem [38]. While the AIM problem cannot be solved rigorously, several levels of approximations exist. The most readily available such method is the assignment of atomic spin from a Mulliken [39] or Löwdin [40] population analysis. These techniques partition a molecular wave function, described by a linear combination of atomic orbital (LCAO) basis functions, into atomic contributions based on which atom each basis function is centered on. That makes Mulliken or Löwdin partial charges strongly basis set dependent, and by way of the basis set also dependent on the geometry. Furthermore, such a partitioning of charge density is highly ambiguous in the interstitial region between atoms in a molecule, where basis functions from neighboring atoms overlap. This spuriousness leads to unphysical, inconsistent variations in the calculated atomic spins [41], which in turn causes large statistical scatter in a fit on the form of Eq. (2) as described above, and a tendency for an unrestricted fitting algorithm to produce negative c_e coefficients.

A more rigorous approach, based on the partitioning of charge density by surfaces where the charge density is stationary in space, is the so-called Bader partitioning [42]. This method, like the calculated molecular charge density it takes as input, is not basis set dependent when converged with respect to the basis set. The Bader method significantly improved the fit results over Mulliken or Löwdin population analysis, with further minor improvements when using an improved grid integration method [43]. However, the highest quality fits, characterized by small statistical scatter, numerical stability, and consistently positive c_e coefficients were obtained with a method [44] partitioning the Voronoi deformation density (VDD). All of the density partitioning AIM methods were

employed using the BADER program (version 0.95a) developed by Henkelman *et al.* [45].

In summary, the calculations were carried out as follows: for each molecule, the fully optimized geometry was calculated for the neutral and cationic molecule. Then the g -tensor and molecular spin density of the resulting geometries were obtained in separate single-point calculations. The spin density was then partitioned into atomic spins by the BADER program using the VDD method, which in turn were fed into the fitting procedure described in the previous section.

III. RESULTS AND DISCUSSION

In this section, all first-principles and fit results are presented and discussed in context. Section III A presents all predictions of g -tensor shifts from DFT. These results are then analysed in terms of our ansatz of a linear dependence of Δg on the local atomic spin populations in Sec. III B. Our ansatz is further applied and validated in the special cases of Δg shifts upon OSC alkylation and in the long charge dwell-time limit. These results are presented and discussed in Secs. III C and III D, respectively.

A. DFT g -tensor shifts: general trends and comparison to experiment

All isotropic g -tensor shifts calculated using DFT for the 78 distinct variations of chemical composition, geometry, and charge-state geometry are presented in Table I, in units of parts per million (ppm). The dominance of the $\Delta g^{\text{OZ/SOC}}$ term in the Δg of these molecules is striking, with the RMS sum of the relativistic mass- and gauge-correction terms of Eq. (1) a negligible 88 ppm. Therefore, for all intents and purposes, the shifts in Δg of these molecules are entirely due to a shift of $\Delta g^{\text{OZ/SOC}}$, highlighting the influence of SOC on Δg . In the following, the labels Δg and $\Delta g^{\text{OZ/SOC}}$ are in parts used interchangeably.

Beginning with the single chalcogen pair molecules [Fig. 1(a)], we see (a) a reduction in Δg with increasing size of the conjugated moiety, (b) a change in Δg upon alkylation of the molecules, similarly diminishing with the size of the conjugated moiety, and (c) identical trends in the sulfur- and selenium-based molecules, up to a roughly uniform scaling factor.

In BTBT, DNTT, and DATT, the size of the conjugated moiety increases from one to two and three pairs of phenyl rings, respectively (see Fig. 1). This increase changes Δg , both quantitatively, in the magnitude of shifts, and qualitatively, in the effect of alkylation: the g -shift in pure BTBT is approximately 9% greater than in pure DNTT, which in turn is 31 % greater than in pure DATT. A visual analysis of the corresponding differences in calculated spin density similar to that of Fig. 2 shows the spin density delocalizing over the entire conjugated moiety, and therefore concentrating less where the orbital angular momentum is greatest, at the central chalcogen atom pair. The resulting reduction in effective molecular SOC reduces the g -shift.

The effect of alkylation of these molecules also strongly depends on the extent of the conjugated system. In BTBT, the spin density is strongly confined to the conjugated moiety.

TABLE I. Isotropic g -tensor shifts Δg calculated using DFT for all molecules studied here, in units of ppm. In column 2, available experimental measurements of Δg . In columns 3–5, theoretically calculated g -tensor shifts Δg_0 in charge-neutral geometries, the corresponding $\Delta g_0^{\text{OZ/SOC}}$ terms, and the change in Δg in the cationic geometry. The cationic g -tensor shift Δg_{+1} can consequentially be obtained by adding columns 3 and 5.

Molecule	Exp. [1]	Δg_0	$\Delta g_0^{\text{OZ/SOC}}$	$\Delta g_{+1} - \Delta g_0$
benzene	-	137	173	-1
pentacene	311	352	346	-7
rubrene	309	81	73	291
BTBT	2141	2238	2216	-327
C8-BTBT	1087	1107	1109	-342
C8s-BTBT	-	2828	2812	-426
BSBS	10010	14255	14129	-2502
C8-BSBS	6322	6773	6696	-3005
C8s-BSBS	-	16677	16548	-2794
DNTT	1959	2073	2035	-164
C8-DNTT	1657	1794	1778	-222
C8s-DNTT	-	1769	1754	-223
DNSS	9772	10414	10289	-1019
C8-DNSS	-	8760	8662	-1391
C8s-DNSS	-	8526	8429	-1312
DATT	-	1598	1553	-112
C8-DATT	-	1481	1459	-123
C8s-DATT	-	1527	1506	-107
DASS	-	7031	6911	-638
C8-DASS	-	6415	6321	-707
C8s-DASS	-	6620	6526	-589
L-DTBTBT	-	4176	4128	-436
C8-L-DTBTBT	3514	4180	4143	-459
C8s-L-DTBTBT	-	4166	4105	-350
L-DSBSBS	-	23265	23082	-2719
C8-L-DSBSBS	-	23527	23353	-3178
C8s-L-DSBSBS	-	23082	22882	-2070
C-DTBTBT	-	419	383	-43
C8-C-DTBTBT	354	237	231	-59
C8s-C-DTBTBT	-	802	759	-111
C-DSBSBS	-	2498	2395	-793
C8-C-DSBSBS	-	1117	1041	-769
C8s-C-DSBSBS	-	4672	4547	-1223
L-DSBTBT	-	15723	15619	-1637
C8-L-DSBTBT	-	16329	16233	-1642
C8s-L-DSBTBT	-	17149	17032	-1599
C-DSBTBT	-	3274	3213	-270
C8-C-DSBTBT	-	1376	1343	-38
C8s-C-DSBTBT	-	5297	5242	-1041

Upon alkylation, spin leaks out onto the alkyl chain and depletes from the chalcogen atom pair, causing a $\sim 50\%$ reduction in the g -shift. Shifting the alkyl chain to the adjacent bonding site, corresponding to a spin density minimum, instead further concentrates spin density on the chalcogen pair, resulting in a $\sim 50\%$ increase in Δg , with the pure BTBT Δg as a baseline. This happens despite the identical chemical composition of C8- and C8s-BTBT.

While alkylation similarly suppresses the g -shift in DNTT and DATT, the effect becomes weaker with increasing size of the conjugated moiety, and the qualitative difference between

alkylation at the two sites vanishes, consistent with a weaker interaction between alkyl chain and spin density as the latter becomes less confined and more delocalized. The effect of substitution of sulfur with selenium roughly amounts to a uniform increase in magnitude of shifts, consistent with a greater orbital angular momentum but otherwise similar chemistry of the heavier chalcogen.

In the dual chalcogen pair molecules [Fig. 1(b)], the molecular geometry has a very large influence on the g -shift (see Fig. 2). In linear DSBSBS (L-DSBSBS), the calculated spin density shows an alternating pattern of maxima and minima (blue and red contours in Fig. 2, respectively), with large weight on both chalcogen atom pairs. The g -shifts are comparatively large, and alkylating the molecule at either a spin maximum or minimum has little to no effect.

By shifting the outer chalcogenophene ring pair by a single bonding site, but maintaining the exact same chemical composition, the picture changes to the opposite: in curved DSBSBS (C-DSBSBS) the pure g -shift is *an order of magnitude* smaller than in L-DSBSBS, and alkylating at a spin density maximum (minimum) approximately doubles (halves) Δg . This is because the spin density of C-DSBSBS has almost no weight on the chalcogens, but heavy weight at the alkyl chain bonding site. Again, this causes spin density to leak onto the alkyl chain, reducing the spin at the chalcogens, and therefore reducing the effective molecular SOC.

Again, comparing to the corresponding sulfur-substituted molecules (L- and C-DTBTBT), we see the very same pattern, albeit reduced in magnitude, consistent with chalcogen weight appearing as a roughly uniform scaling of Δg . In the curved mixed dual chalcogen pair molecules (C-DSBTBT), the same pattern again emerges, but at absolute Δg magnitudes between those of C-DTBTBT and C-DSBSBS— g -shifts are “averaged” between the sulfur and selenium chalcogen pair. However, whereas the Δg of L-DTBTBT and -DSBSBS are largely unaffected by alkylation, the Δg of L-DSBTBT increases, particularly when alkylating at the shifted bonding site.

Comparing to the 11 already published [1] experimental numbers, we note that these refer to molecules with alkyl chains 8, 10, and 12 methylene units long, whereas the theoretical structures all have 8-unit chains. Since test calculations showed no variations of g -tensor shifts beyond a chain length of about four units, this comparison is valid.

Theoretical predictions generally compare very well to the experimental data, with the lone exception of the BSBS molecule. The RMS error to the experiment of the theoretical predictions is 342 ppm when excluding BSBS, which at this level of theoretical approximations can be considered negligible. When including the BSBS number, the RMS error increases to 1321 ppm. As evident from Table I and elaborated upon in Sec. IIID, the effect of longer charge dwell time is a suppression of Δg across all molecules studied here. For BSBS, the DFT prediction error of some 42% in the short charge dwell-time limit (neutral molecular geometry) shrinks to approximately 17% in the long charge dwell-time limit, providing a possible explanation for the discrepancy in the comparison to experiment for this molecule. Still, 17% dwarfs the error (7%, 451 ppm) in, for example, the prediction for the short charge dwell-time limit of C8-BSBS, for which the long charge dwell-time limit is a very poor approximation

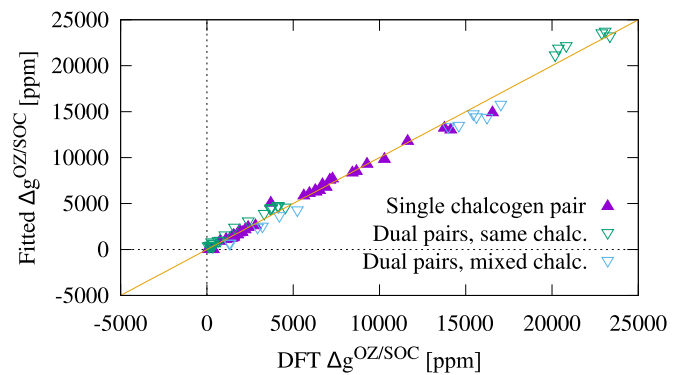


FIG. 3. Correlation plot of $\Delta g^{\text{OZ/SOC}}$ terms fitted on the form of Eq. (2). The fit was done separately for a single chalcogen pair (solid, magenta triangles) and dual chalcogen pair molecules (empty, inverted triangles). Dual pair molecules with same and mixed chalcogens were fitted together, but are colored differently to show the identical validity of the approximation regardless of chalcogen composition. The R^2 for the single- and dual-chalcogen pair statistics are 0.990 and 0.991, respectively.

(38% error). The theoretical method used is identical for all molecules, suggesting an inconsistency in the experimental BSBS measurement not well described by the single-molecule approximation.

B. Validation of linear ansatz model

While the picture thus far is well explained by a visual analysis in terms of differences in spin density at high orbital angular momentum atoms on the form of Fig. 2, a quantitative analysis on the form of Eq. (2) is far more exhaustive. A straight fit of all local atomic spin populations versus theoretically predicted g -shifts yields a (for a strictly linear statistical hypothesis) low R^2 of 0.949. Furthermore, despite using the high-quality Voronoi density partitioning method, this fit is numerically unstable for the carbon c_e , which comes out negative. In other words, the single fitting set of all molecules studied here is poorly described by the ansatz of a linear dependence of Δg on strictly localized atomic spin populations.

This is because the single-pair molecules have a single (C_{2h}) symmetry unique chalcogen atom, but the dual-pair molecules have two. The resulting difference in chalcogen-chalcogen interactions may shift c_e , since it describes both one- and two-body spin-orbit interactions determining $\Delta g^{\text{OZ/SOC}}$ as a single, local, effective coefficient. Fitting the dual-pair molecules separately yields a high R^2 of 0.991. This fit is shown as inverted, empty triangles in a correlation plot in Fig. 3. Importantly, and further underscoring the insight that geometry is the key in the variations of Δg in the dual-pair molecules, all dual-pair molecules are fitted together. That is, the mixed chalcogen dual pair molecules (e.g., L-DSBTBT) are described just as well by the model as the pure sulfur (e.g., L-DTBTBT) or selenium (e.g., L-DSBSBS) ones. Highlighting the similar performance of the linear ansatz for all dual-pair molecules, the empty inverted triangles of same and mixed chalcogen pair molecules are differently colored in Fig. 3.

The C8- and C8s-BSBS molecules produce negative carbon c_e when included in the fitting set of the other single-pair

TABLE II. Average c_e coefficients of Eq. (2) obtained in the fit of Fig. 3, and the corresponding standard deviation (SD) and relative standard deviation (RSD) of c_e over the fitting set (see text).

Element	Avg. c_e	c_e SD	RSD (%)
Single chalcogen pair molecules			
C	1.28×10^{-4}	1.59×10^{-5}	12
S	7.76×10^{-3}	5.63×10^{-5}	0
Se	3.35×10^{-2}	1.16×10^{-4}	0
Dual chalcogen pair molecules			
C	3.06×10^{-4}	1.66×10^{-5}	5
S	1.03×10^{-2}	1.08×10^{-4}	1
Se	4.66×10^{-2}	1.17×10^{-4}	0

molecules in the procedure described at the end of Sec. II B. We therefore exclude these two from the fitting sets of the other molecules. With an otherwise unmodified fit procedure, the fitted single-pair molecule statistic also yields a very high R^2 of 0.990, which is shown as filled triangles in Fig. 3.

Just as with the relatively large error in Δg predicted by DFT for BSBS, the perfect consistency of the theoretical method only allows for speculation as to why C8- and C8s-BSBS are outliers in our linear model. We conjecture that the strong confinement of the electron hole on the small BSBS moiety leads to stronger nonlocal interactions of the spin density when an alkyl chain is added, in violation of the local, linear dependence of Δg underlying our quantitative ansatz.

The average c_e obtained in the fit are presented in Table II. Since each molecule is excluded from the fitting set when calculating its fitted $\Delta g^{\text{OZ/SOC}}$, the c_e vary slightly for each molecule. However, the standard deviations are generally small, with relative standard deviations for the chalcogens below 1%. Standard deviations are largest for the carbon coefficients, which being smallest suffer most from limited numerical precision in the output data. Notably, the difference in chalcogen-chalcogen interactions between the single- and dual chalcogen pair molecules appears as a general increase in the c_e for the dual pair molecules.

In summary, the linear ansatz of Eq. (2) is both highly successful in quantitatively describing the dependence of g -shifts on changes in local spin density at high orbital angular momentum atoms, yet sensitive to differences in nonlocal interactions violating the premises of the model.

C. Alkylation

As already briefly discussed above, the effect on predicted g -shifts of functionalization with an alkyl chain is particularly dramatic. Alkylation shifts vary from small to negligible shifts independent of alkyl chain bonding site in, e.g., DATT, DASS, L-DTBTBT, and L-DSBSBS, to shifts in on the order of the g -shift of the pure molecule, either positive or negative depending on the alkyl chain bonding site, as in, e.g., C-DTBTBT or C-DSBTBT. The expectation of merely improving structural properties or solubility of these molecules by adding alkyl chains clearly does not hold here.

In order to elucidate the mechanism behind the alkylation shift, and showcase the utility of our linear ansatz, we reapply the model to the alkylation shifts analogous to Eq. (2). In Fig. 4,

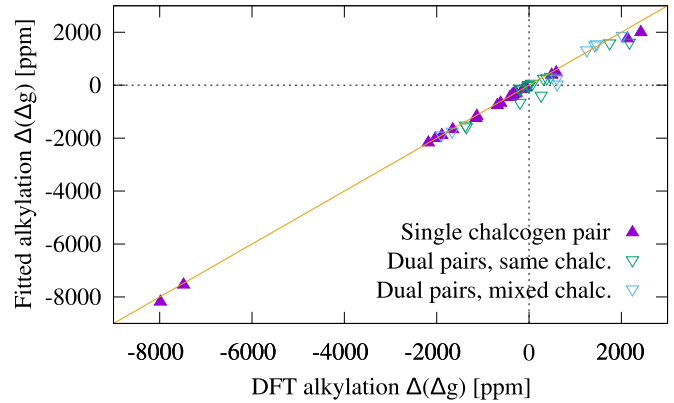


FIG. 4. Correlation plot of a fit of the shift in Δg upon alkylation of molecules against the corresponding change in local chalcogen spin population, analogous to Eq. (2) and Fig. 3. See Fig. 3 for the plot legend. R^2 of the entire statistic shown is 0.988.

we have fitted the change in Δg [i.e., $\Delta(\Delta g)$] upon alkylation as a linear function of the corresponding change in local spin population at the chalcogen atoms only. The differences to the fit to Δg itself in Fig. 3, is that we do not fit single- and dual-pair molecules separately, nor do we consider changes in spin populations at carbon atoms.

Despite these simplifications, our ansatz works exceedingly well for the alkylation shifts, with an R^2 of the (entire) fit in Fig. 3 of 0.988. This high correlation allows us to identify the mechanism of the alkylation shift as the alkyl chain pushing or pulling spin density onto the chalcogen atoms. The validity of this statement is notably independent of number or composition of the chalcogen atom pairs, geometry, charge confinement, etc. Furthermore, and counterintuitively, it shows how (a) an otherwise relatively chemically inert functional group can modulate the effective molecular SOC by bonding site alone, and therefore (b) that functional groups may work as a key design element in the tuning of g -tensors in these and similar OSC molecules. This finding is also in line with the view of SOC in light organic molecules as generally dependent on their electronic structure [8], as opposed to chemical composition alone.

D. Charge dwell time

The molecules studied in this work are nonmagnetic, and only acquire a spin (and therefore, a g -tensor) when ionized. We compare theoretically calculated g -shifts of ionized single molecules to experimental measurements. In an experimental sample or OSC material, these molecules form ensembles through which free charge carriers (introduced via, e.g., doping) diffuse with an average rate τ^{-1} .

If the average time τ spent by a charge at a single molecule (also known as the charge dwell time) is short, the geometry of the neutral molecule is a good approximation of the average real molecule in the experimental sample (see Fig. 5). If instead the dwell time is long, the ionic geometry, or molecular geometry relaxed with respect to the charge of the molecule, is a better approximation. We may consequentially understand the effect of charge dwell time on experimental measurements by calculating Δg in both geometries.

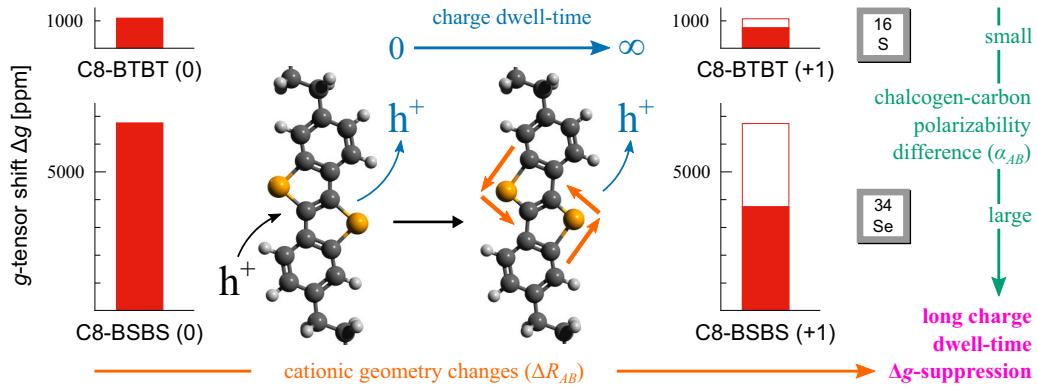


FIG. 5. Illustration of the influence of charge dwell-time effects on the g -tensor shift. See Sec. III D. If a charge—here an electron hole h^+ —dwells for sufficiently long at a molecule, it relaxes to the ionic geometry, causing changes in the bond lengths R_{AB} , shifting the push-pull charge balance along the bonds. While ΔR_{AB} are nearly identical in C8-BTBT and C8-BSBS, the relatively greater polarizability of selenium more strongly pulls electrons toward (pushes holes from) the chalcogen, causing spin density depletion at the same, and a stronger suppression of the g -shift in C8-BSBS than in C8-BTBT [see Eq. (4)].

As evident from Table I, Δg decreases for long dwell times for all molecules, which we from our ansatz [Eq. (2)] know to be synonymous with spin density depletion at the chalcogen atoms. The lack of an obvious pattern in the agreement between experimental measurements and theoretical predictions in either dwell-time limit suggests that the number of experimental measurements is insufficient to describe differences in charge diffusion dynamics between the molecules. While the Δg suppression is strongest in some of the selenium-based molecules, the magnitudes of the effect are not consistent with a mere uniform scaling factor when comparing to the sulfur-based molecules. In fact, the reduction in spin density upon cation structural relaxation of all molecules studied here is roughly twice as large at selenium as at sulfur.

This phenomenon can be understood using concepts from push-pull chemistry, specifically intramolecular charge transfer (ICT) theory. As the geometry of a charged molecule changes (see Fig. 5) to accommodate that charge, the charge equilibrates along molecular bonds by ICT. We may understand the charge balance along these bonds by comparing them to diatomic molecules of elements A and B. In the so-called electronegativity equalization approximation (EEA) [46,47], the equilibrium charge Q_{AB} due to ICT in such a molecule is approximated as

$$Q_{AB} = \frac{\Delta\chi_{AB} \cdot \alpha_{AB}}{R_{AB}^2}, \quad (4)$$

where $\Delta\chi_{AB}$ is the difference in electronegativity (EN) between A and B, α_{AB} the polarizability of AB, and R_{AB} the interatomic bond length. Equation (4) allows us to analyze Q_{AB} in terms of estimates of atomic EN and polarizability parameters. Since these parameters effectively depend on the (covalent) bonding state, such an analysis is not strictly valid. Additionally, one should be aware of the limitations of a comparison between a diatomic molecule and an internal bond in a larger molecule.

Still, on a qualitative level, the EEA is useful here. In pure hydrocarbons, ICT will only occur between carbon atoms of similar EN and polarizability. Therefore changes in local spin populations upon cationic relaxation in pentacene and

rubrene almost entirely depend on changes in bond lengths R_{AB} . Such changes are small in the hydrocarbons studied here. Consequentially, so is the suppression of Δg .

In the chalcogenophene molecules, the change in chalcogen spin populations will depend on the change in bond lengths, but also the relative difference in EN and polarizability between the chalcogens and carbon. Carbon, sulfur, and selenium atoms all have similar EN of $\chi_C = 2.55$, $\chi_S = 2.58$, and $\chi_{Se} = 2.55$ Pauling, respectively [48]. However, their polarizabilities differ significantly, at $\alpha_C = 1.76$, $\alpha_S = 2.90$, and $\alpha_{Se} = 3.77 \text{ \AA}^3$, respectively [49].

The greater polarizability of the chalcogens pushes positive charge towards the surrounding carbon atoms, and vice versa for negative charge. Since the charge carries the spin, Δg upon cation structural relaxation decreases for all chalcogen containing molecules. The corresponding changes in carbon-chalcogen bond lengths in the sulfur-based molecules are nearly identical to those in their selenium-substituted analogues. Therefore the greater spin depletion at selenium atoms evidenced by the stronger Δg suppression, can only be explained by the larger polarizability of selenium compared to sulfur. These results highlight how the ICT properties and charge dwell-time can be exploited in conjunction to tune the g -tensor of an OSC.

IV. SUMMARY

Arguably, the strongest argument for the use of OSCs in spintronic applications is their great potential for relatively easy tuning for a specific purpose. We have studied a class of high-mobility chalcogenophene OSCs based on a simple structural theme of phenyl and chalcogenophene rings functionalized with alkyl chains using density functional theory. Our results show dramatic variations—synonymous with potential tunability—of the molecular g -tensor shift Δg with changes in molecular geometry, extent of the conjugated moiety, chalcogen weight, alkyl chain bonding, and charge dwell time when ionized. With a single exception, our predictions match available experimental data very well.

Our calculations show that Δg in this OSC class is almost entirely determined by the molecular SOC. We analyze our results using a model assuming a linear dependence of the effective molecular SOC on local atomic spin populations. This model accurately reproduces DFT Δg when fitted to atomic spins, explaining variations in Δg in terms of the overlap of molecular spin and orbital angular momentum distributions—in other words, the effective SOC. We apply our model to explain the large and counterintuitive variations in Δg with alkyl chain bonding, as well as the effect of structural relaxation of the molecules when positively charged.

In general, this work presents a methodological recipe for a first-principles theoretical analysis of aspects of molecular

SOC: the concept of describing the molecular SOC as dependent on localized atomic spin populations can be applied to numerous phenomena beyond g -tensor shifts. In particular, our work exhaustively explains how and to what degree tuning of the g -tensor in this class of OSCs is possible.

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